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Extensional viscosity of w/o emulsions

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Abstract

The opposed nozzles configuration was used to measure the extensional viscosities of water-in-oil emulsions of dispersed volume fractions varying between 5% and 30%. The two Newtonian type mineral oils with dynamic viscosities about η = 0.2182 and 0.0443 [Pa·s] were used. All emulsions were prepared with sorbitan monooleate (Span 80) as emulsifier. The results obtained for extensional viscosity of w/o emulsions show that only at very low concentrations of dispersed phase values of the Trouton ratio ($Tr = \eta_E/\eta$) are approximately constant (in range of 7-11) while for pure oil are slightly lower (3-6). Additionally, the Trouton ratio is independent of oil phase viscosity in the range of water phase concentration from 5 to 10%. For 20% and higher concentration of disperse phase the extensional viscosity rises with increase of a nozzle diameter. Presented experimental results indicate that the opposing nozzles rheometer used in this work is not a suitable device for measuring the extensional viscosity of viscoplastic fluids.

Keywords: Extensional viscosity; Trouton number; w/o emulsions; span

1. Introduction

Emulsions are mixtures of two immiscible liquids, where the droplets of one phase are suspended in a continuous phase of the second one. There are mainly two types of emulsions: oil-in-water (o/w) where a dispersed oil droplets are in a continuous water phase, and water-in-oil (w/o) type while water droplets are dispersed in continuous oil phase. Insignificant amount of literature data related to the extensional

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flow of emulsion systems (however increasing recently) indicates that it may be important property from both points of view which are: properties of final product and description of flow pattern.

Nomenclature

R	radius of nozzle
M	torque
L	arm length
h	distance between the nozzles
$\dot{V}$	flow rate
$\dot{\varepsilon}$	extension rate
Tr	Trouton number
η_E	extensional viscosity
η	shear viscosity

W/O emulsions are less popular than the o/w, but the extensional flow of the w/o emulsions can be observed in everyday activities such as spreading butter on bread. Moreover, w/o emulsions are usually used in food [1,2], cosmetic [3], pharmaceutical [4] and petrochemical industries. Therefore, there is quite many an information available in open literature, however for complete characterization of this class of fluids it is necessary to evaluate their behavior in an extensional flow. Rheological properties of w/o emulsion in shear flow are subject of many studies [5,6], but in the literature only a few information about the extensional viscosity of the emulsion are presented [7,8].

Anklam et al. [7] used the opposed nozzles configuration to measure the extensional viscosities of water-in-oil emulsion. Authors [7] showed that the rheological properties of w/o emulsions in the extensional flow strongly depend on concentration of the dispersed phase. In the case of emulsions with dispersed phase concentrations ranging from 30 to 60 vol.-% the Trouton ratio was approximately equal to three. In the case of emulsions with a higher content of the dispersed phase, the measured values of extensional viscosity strongly depended on the diameter of nozzles used for measurement. On that basis, Anklam et al. [7] concluded that the opposing nozzles rheometer was not a suitable device for measuring the extensional viscosity of concentrated emulsions.

Article published by Niedzwiedz et al. [8] presented the measurements of the concentrated water in oil emulsions in the extensional flow using a Capillary Breakup Elongational Rheometer (CaBER). Researchers [8] studied effects of disperse volume fraction, droplet size, and continuous phase viscosity on the flow properties. They have shown that at a critical volume fraction φ_c, when the droplets are densely packed and start to deform, shear and as well as extensional flow properties change drastically. Shear flow curves exhibit strong shear thinning and an apparent yield stress. For the emulsion series investigated in that work covering two orders of magnitude in the yield stress a constant ratio $\tau_{y,e}/\tau_{y,s} \approx 3$ was found (where $\tau_{y,s}$ is the yield stress in shear flow and $\tau_{y,e}$ is the yield stress in extensional flow).

The extensional flow of emulsions was also raised in the work of Akay [9]. It reported the phenomenon of phase inversion from w/o to o/w, which were not forced by thermodynamic changes but by stretching. The stretching flow of fluid had been established in static mixer consisting of convergent nozzle, capillary and converging cone. Author of article [9] determined that degree of phase inversion depended on deformation rate and number of static mixers.

In general, the first study of extensional flow is acknowledged to Trouton's 1906 paper [10]. In uniaxial extension, the elongational viscosity η_E is defined as the ratio of the difference between normal stresses τ_{xx} - τ_{yy} to rate of extension $\dot{\varepsilon}$ [11]:

$$\eta_E = \frac{\tau_{xx} - \tau_{yy}}{\dot{\varepsilon}} \tag{1}$$

Trouton [10] found that the proportion between stress and velocity gradient was constant but three times larger than the value he measured in shear. Therefore, the Trouton number has been defined as the ratio between extensional viscosity and viscosity in shear flow:

$$Tr = \frac{\eta_E}{\eta} \cong 3 \tag{2}$$

Measurements of the extensional viscosity are incomparably more difficult than for the shear viscosity. There are many methods proposed for the study of extensional viscosity of fluids. Each of them uses different methods of creating approximated extensional flow and employ different methods for measuring and interpreting the extensional stress. This study focuses on the opposed jets system which has been one of the most popular methods for measurement of extensional flow properties. This method is widely used to measure the extensional viscosity of low-viscous liquids, below 1 [Pa·s] and it is the fundamental apparatus used to study fluids with viscosity comparable to water.

Double stagnation flows generated by sucking or blowing liquid into or from opposed nozzles have been used in the last three decades to approximate uniaxial extensional flow. Firstly, Frank et al. [12] applied that method to chain extension and flow-induced crystallization. Later on, in an extensive study, Mackley and Keller [13] examined flow-induced crystallization of polyethylene melts in such geometry. Using flow visualization as well as birefringence they found that the flow generated between two aligned opposed nozzles is predominantly extensional in nature, but some shear is still present.

Since the beginning of extensional viscosity measurements researchers utilized two different methods of its measurements. Keller et al. [14] and Chow et al. [15] tried to estimate an effective extensional viscosity in opposed-nozzle flow by measuring the pressure drop across the nozzles. At the same time, Fuller et al. [16] proposed an alternative method to measure extensional viscosity based on a force measurement in opposed-nozzle flow. They were the first to correlate quantitatively an apparent extensional viscosity to measurable dynamic quantities in the opposed-nozzle configuration. They measured the force needed to balance the hydrodynamic force exerted by the flowing liquid on one of the nozzles, and moreover related it to the liquid's apparent extensional viscosity through equation [17]:

$$\eta_E = \frac{M}{\dot{\varepsilon} \cdot \pi \cdot R^2 \cdot L} \tag{3}$$

The apparent extension rate in the flow $\dot{\varepsilon}$ was related to the flow rate $\dot{V}$ in one nozzle by following equation (4).

$$\dot{\varepsilon} = \frac{\dot{V}}{\pi \cdot R^2 \cdot h} \tag{4}$$

In this paper the experimental results for water-in-oil emulsion were obtained on an extensional rheometer which uses a stagnant flow between opposing nozzles. This rheometer was build based on own design.

2. Experimental

2.1. Materials and methods

Spans are nonproteic emulsifiers with a higher hydrophobic than hydrophilic character (low HLB). They are sorbitan esters differentiated among themselves by the characteristics of their fatty acid chains. As a general rule, it is accepted that emulsifiers should have more affinity to the continuous phase than to the dispersed one thus, Spans are adequate to formulate this type of emulsions. Span 80 (sorbitan monooleate) was obtained from Sigma-Aldrich (Poland). Mineral oils were obtained from Institute of Petroleum Technology from Kraków in Poland. The two Newtonian type mineral oils with viscosities about $\eta = 0.2182$ and 0.0443 [Pa·s] were used.

2.2. Emulsion preparation

Water-in-oil emulsions were prepared by adding the water phase, drop by drop, to an equal volume of mineral oil containing Span 80 while stirring with Ultra Turrax homogenizer at a speed of 6000 rpm. The measurements were carried out for w/o emulsions in the range of disperse phase concentration ϕ (water phase) varied from 5 to 30 vol.-%. Span 80 was used as an emulsifier and its concentration in all prepared emulsions was equal to 1%.

2.3. Experimental set-up

The rheological measurements in shear flow were carried out using a rotational rheometer Physica MCR 501 produced by Anton Parr (Germany) equipped with cone-plate measuring system. The measuring device was equipped with a temperature unit (Peltier plate) that provided very good temperature control over an extended period of time. All measurement were carried out at $T = 20^\circ$C.

Extensional viscosity measurements were made with an opposed-nozzle device of tailored construction. The scheme of opposed-nozzle rheometer is shown in Fig. 1. That flow geometry with equal flow rates through both nozzles generates a symmetric flow field with the stagnation plane at the midpoint between these nozzles.

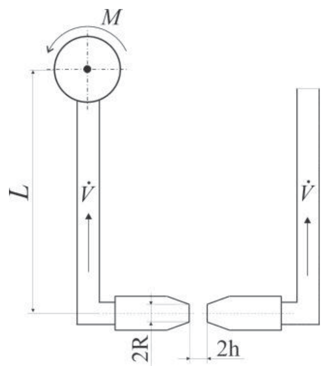

Fig. 1. Schematics of the opposed-nozzle device

During the measurement the fluid was sucked out simultaneously by the two jets with an organized system of two syringes controlled by a computer. One of the nozzles was mounted on a movable arm connected to the torque meter of unique structure delivered by the Roman Pomianowski Laboratory of Electronics (Poland). In measurements three different nozzles with 1, 2 and 3 mm diameter were used. The apparent extensional rates were in the range from 0.9 to 1019 s^{-1}.

3. Results

3.1. Shear flow

Viscosity curves of w/o emulsions made of mineral oil with two different viscosities, namely 0.0443 [Pa·s] and 0.2182 [Pa·s], are presented in Figures 2 and 3, respectively. Presented data show that emulsions are shear-thinning fluids. However, above shear rate of 100 s^{-1} values of viscosity are virtually constant. Moreover, it was observed that viscosities of all emulsions increase with increase of water content.

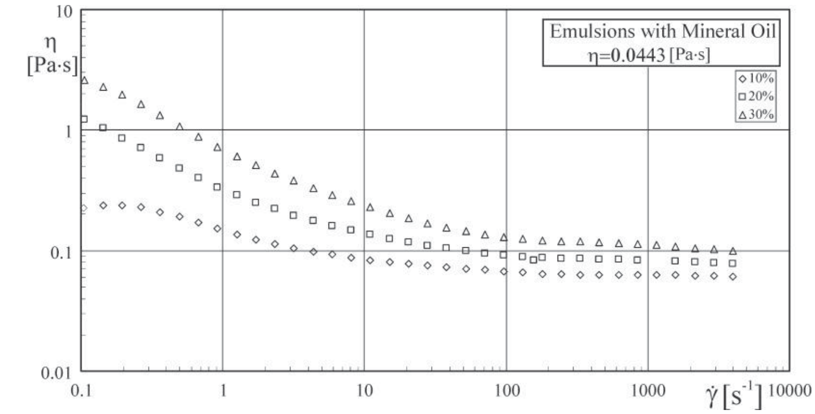

Fig. 2. Viscosity curves for emulsions based on mineral oil with viscosity equal to 0.0443 [Pa·s]

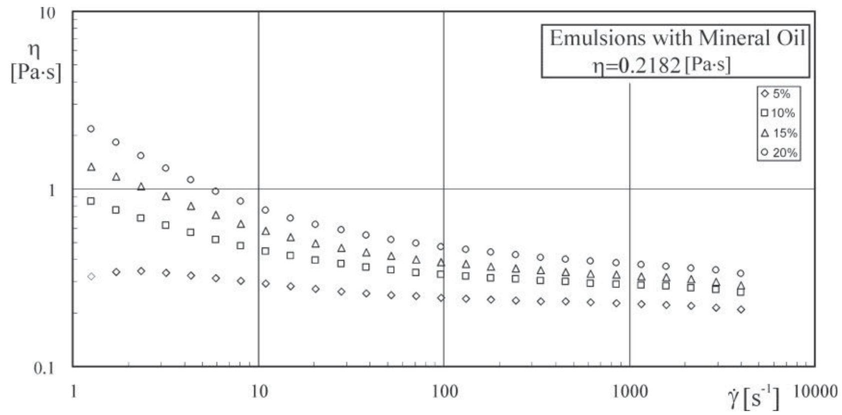

Fig. 3. Viscosity curves for emulsions based on mineral oil with viscosity equal to 0.2182 [Pa·s]

Additional measurements were performed in order to determine whether the studied emulsions exhibit the slip effect. Therefore, flow curves were determined with use of cone-plate (CP60-1, 60 mm) and plate–plate (PP50/TG, 50 mm) geometries with smooth surfaces as well as with rough plate-plate. The gaps varied between 0.8 mm and 1.2 mm. Using a rough plate, the results were similar to those for the measurements of the cone-and-plate and smooth plate-plate geometries Therefore, performed measurements have shown that the all results are independent of the size of the gap. This indicates that the tested emulsions do not show the slip effect. In Fig. 4 comparison between viscosity curves obtained with use of smooth and rough surfaces for emulsions with mineral oil ($\eta = 0.2182$ Pa·s) and water phase concentration equal to 15% is presented.

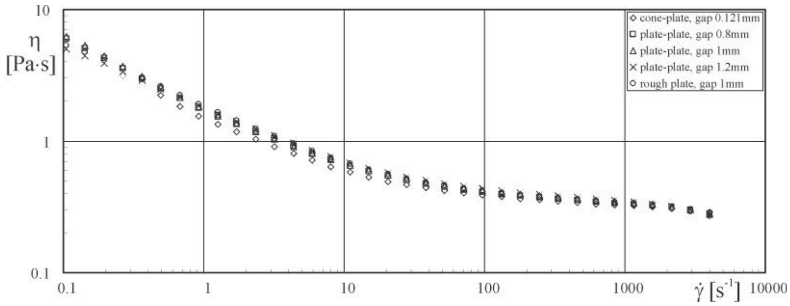

Fig. 4. Comparison of flow curves of emulsions measured with different smooth and rough measurement geometries

3.2. Extensional flow

Figure 5 shows the extensional viscosity curves as a function of the extensional rate for emulsions with various concentrations of the aqueous phase; emulsions are based on oil with a viscosity of 0.0443 [Pa·s].

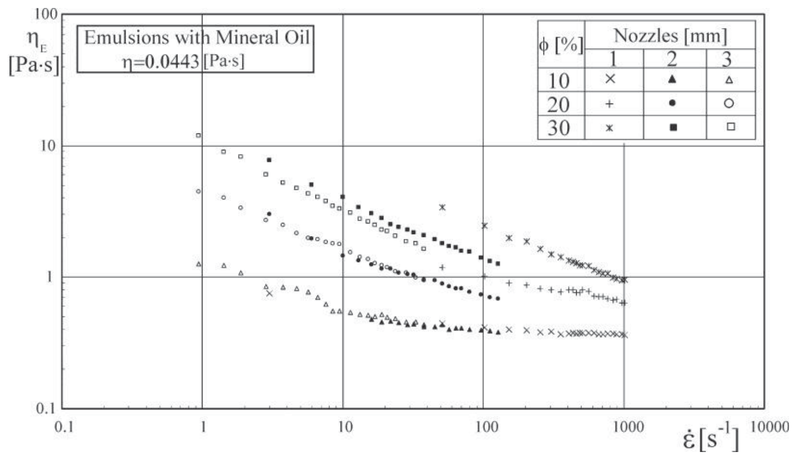

Fig. 5. Extensional viscosity curves for emulsions with water phase concentration of 10%, 20% and 30% based on oil with viscosity 0.0443 [Pa·s]

It is worth to notice that with increasing concentration of the water phase the extensional viscosity increases while it decreases with increasing stretching rate. For the emulsion with water phase concentration of 10% and the stretching speed in range from 30 to 1019 [s^{-1}] the extensional viscosity reaches practically constant value.

Additionally, in the case of that emulsion experimental points obtained with nozzles of different diameters are actually forming one relationship. No such compliance can be observed for the w/o emulsion with higher concentrations of dispersed phase. In the case of emulsions with a concentration of 20% and for nozzle diameter of 1 mm and 2 mm all experimental points also form a relationship, while for the 1 mm nozzle are moved towards higher values. For the emulsion with a concentration of 30% all three experimental series, each one for a nozzle, form separate dependencies

In Fig. 6 the dependency of the extensional viscosity as a function of the stretching rate for the w/o emulsion with oil phase viscosity equal to 0.2182 [Pa·s] is shown. In this case, the extensional viscosity values measured for the nozzle with 1 mm diameter deviate from that of the experimental points at the concentration of the dispersed phase of 15% and 20%.The effect of diameter for extensional viscosity measurements on w/o emulsion with use of a rheometer with opposing jets was previously described by Anklam et al. [7]. Authors of that paper relate the observed effect of nozzle diameter to the occurrence of yield stress. One force could arise from the yield stress of the fluid on the torsion arm of the apparatus. A fluid with a yield stress will not flow unless the applied stress is greater than the yield stress, so a stress at least as great as the yield stress propagates through the beaker, therefore, creates a force on the nozzle arms, because fluid at all points within the beaker flows towards the nozzles. Explanations given by Anklam et al. [7] apply to a case in which extensional viscosity increases along with nozzle diameter at given stretching rate. In despite to that explanation, it cannot be explained similarly the case in which the experimental results are consistent for nozzles with 2 and 3 mm diameters while for 1 mm are significantly different. Moreover, this effect is not related to inertia, since it occurs for the emulsions with higher viscosity where its impact should be smaller.

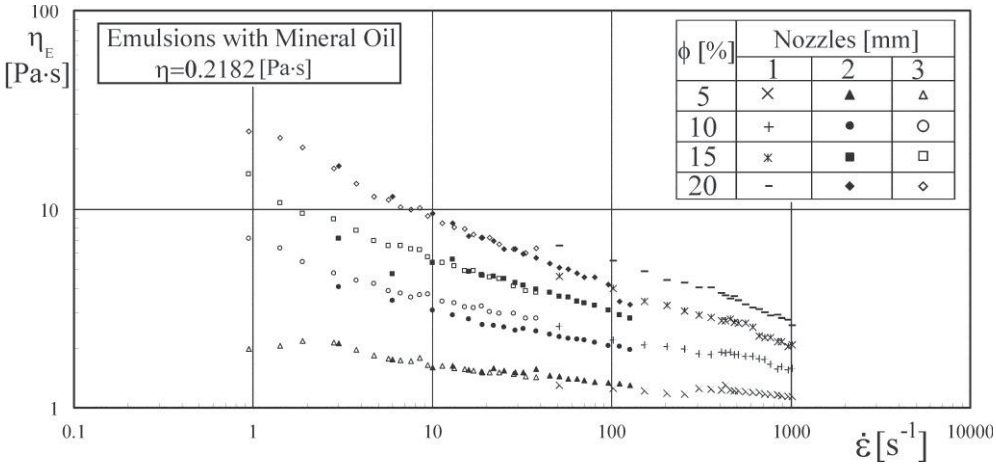

Fig. 6. Extensional viscosity curve for emulsions with oil 02182 [Pa·s] and water phase concentration of 5%, 10%, 15% and 20%

The dependencies of the shear viscosity in function of shear stress of studied emulsions are given in Figures 7 and 8. These data suggest that in the case of emulsion with the concentration of 30% and viscosity of oil 0.0443 [Pa·s] insignificant value of yield stress is observed ($\tau_o \approx 0.25$ [Pa]). As previously mentioned only in this case the experimental points form three different series depending on the diameter of nozzle. Interestingly, based on data presented in Fig. 8 the estimated value of yield stress for the emulsion with a concentration of 20% is about 1.2 [Pa]. This value is much higher than that of the emulsion with concentration of 30% and oil phase viscosity 0.0443 [Pa·s]. Despite this, the experimental points for emulsion with concentration of 20% for nozzle diameters of 1 mm and 2 mm form a single relationship.

Summarizing results described in this subsection and its explanations the imperfections in measurement technique for extensional viscosity utilizing the flow between two opposing nozzles are reviled. For further considerations in this work only these measurement series were utilized for which the consistency of results between minimum two nozzles of different diameters were found.

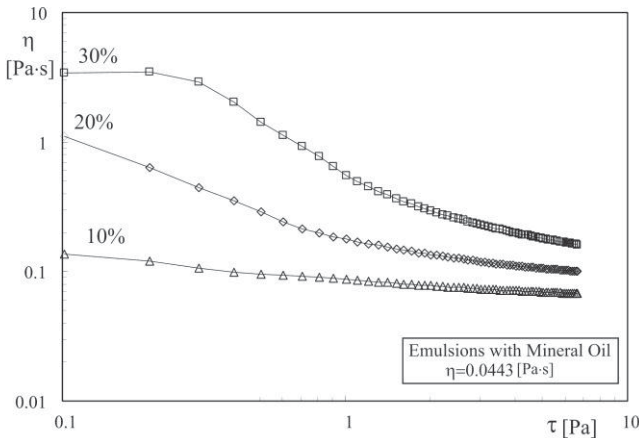

Fig. 7. Dependencies of $\eta = f(\tau)$ for emulsions with mineral oil (η_{oil} = 0.0443 [Pa·s])

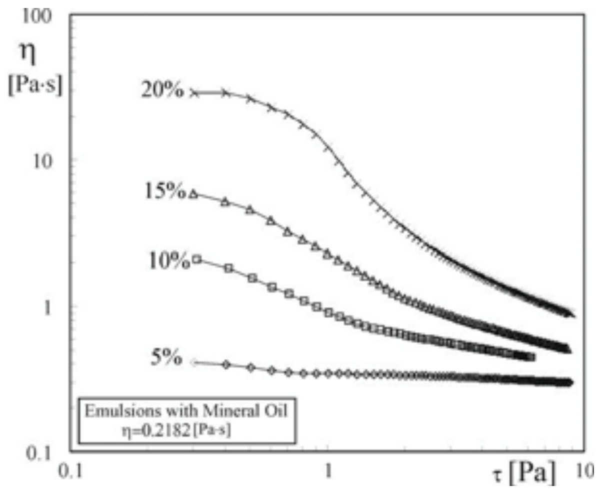

Fig. 8. Dependencies of $\eta = f(\tau)$ for emulsions with mineral oil (η_{oil} = 0.2182 [Pa·s])

Figure 9 shows the comparison of two dependencies $\eta = f(\dot{\gamma})$ and $\eta_E = f(\dot{\varepsilon})$ for two emulsions with 10% of water phase. From the qualitative point of view corresponding experimental series obtained in the stretching and shear flow are analogical. Both, extensional and shear viscosity of the fluid analysed decrease with increasing strain rate.

However, there are quantitative discrepancies. Dependency between the ratio of extensional and shear viscosities (Trouton number) and strain rate is presented in Fig. 10. Due to comparability, the experimental points obtained for mineral oil (Newtonian fluid) of viscosity η = 0.044 [Pa·s], which were performed for the nozzle with a diameter of 1 mm, are also given in that Figure. Experimental values of the Trouton number are within the limits from 3.2 to 3.6 (literature data for similar facilities and ranges are within the range from 2.9 to about 4.6). In the case of the extensional viscosity measurements using the rheometer with opposing jets it is not possible to fully eliminate the influence of shear and inertia on the measured torque value, which could explain the observed derogation from the theoretical value for Newtonian fluids which is Tr = 3.

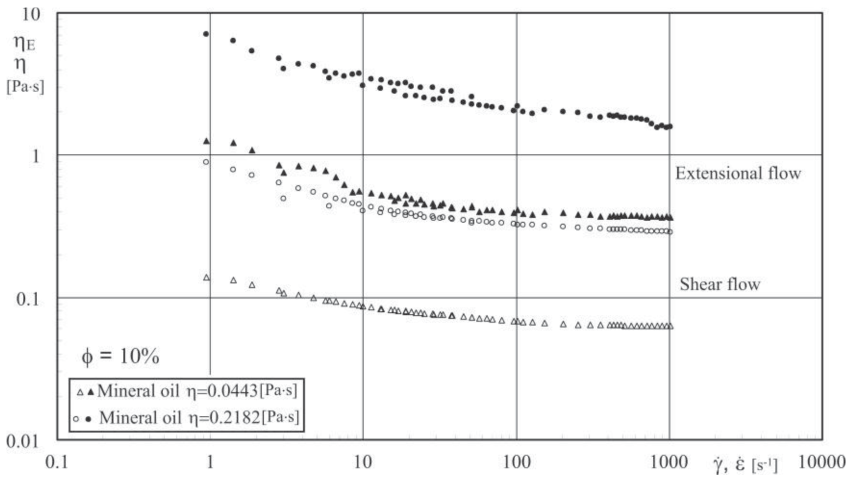

Fig. 9. Comparison of extensional and dynamic viscosity for emulsions with water phase concentration equal to 10%

Trouton ratio for Newtonian fluid is independent of strain rate. A similar relationship was observed for the emulsions with 10% of water phase, but the Tr number in this case reaches value greater than that for Newtonian fluids and the extension rate of 100 do1019 s^{-1}, which is about 7.8.

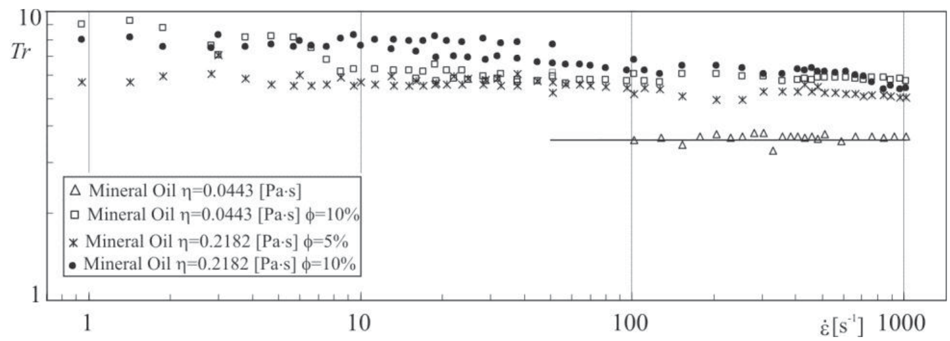

Fig. 10. Trouton ratio for emulsion and Newtonian oil

Effect of concentration of the dispersed phase (5 to 20%) on the course of Trouton number in function of strain rate is shown in Figure. 11. In all cases presented cases, the value of Tr is independent of strain rate, and increases with increasing water content. For the emulsion with concentration of 5% the $Tr \approx 7.6$, while for 20% increases to 11.4. In addition, the data presented in Figure 11 show that the Trouton ratio does not depend on the viscosity of the oil phase. For example, the mean numbers of Tr for emulsions with 20% of water phase and oil phase having viscosity of 0.2182 [Pa·s] and 0.0443 [Pa·s] are respectively 11.35 and 10.92.

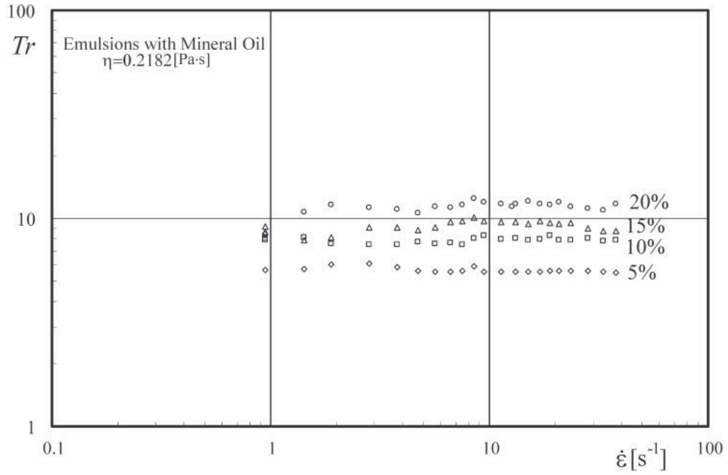

Fig. 11. Influence of dispersed phase concentration (5% to 20%) on course of Trouton number in function of strain rate

4. Conclusions

The extensional properties of water-in-oil emulsions were studied using opposed nozzle rheometry of our own design. The results obtained for extensional viscosity of w/o emulsion show that only at very low concentrations of dispersed phase Trouton ratio ($Tr = \eta_E/\eta$) is approximately constant (7-11) and has a similar (slightly higher) value as for pure oil (3-6). Moreover, the concentration of the water phase from 5 to 10% values of Trouton ratio are independent of the viscosity of the oil phase. For higher concentrations of dispersed phase (above 20%) the extensional viscosity increases with increasing diameter of the nozzle. These data indicate that the opposing nozzles rheometer is not a suitable device for measuring the extensional viscosity of viscoplastic fluids.

Acknowledgements

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References

[1] Norton J, Fryer P, Parkinson J, Cox PW. Development and characterisation of tempered cocoa butter emulsions containing up to 60% water. *J Food Eng* 2009;**95**:172-178.

[2] Aguilera JM, Lillford PJ. *Food Materials Science: Principles and Practice* (Food Engineering Series). 1st edn. London Springer UK; 2007.

[3] Le Re´ve´rend BJD, Taylor MS, Norton IT. Design and application of water-in-oil emulsions for use in lipstick formulations. *Int J Cosmet Sci* 2011;**33**:263-268.

[4] Akhtar N, Khan BA, Khan MS, Mahmood T, Khan HMS, Iqbal M, Bashir S. Formulation development and moiturising

effects of a topical cream of *Aloe vera* extract. *WASET* 2011;**75**:172-180.

[5] Malkin AY, Masalova I. Shear and normal stresses in flow of highly concentrated emulsions. *J Non-Newtonian Fluid Mech* 2007;**147**:65-68.

[6] Bernard P, Binks JH, Clint Whitby CP. Rheological behavior of water-in-oil emulsions stabilized by hydrophobic bentonite particles. *Langmuir* 2005**;21**:5307-5316.

[7] Anklam MR, Warr GG, Prud'homme RK. The use of opposed nozzles configuration in the measurements of the extensional rheological properties of emulsions. *J Rheology* 1994;**38**:797-810.

[8] Niedzwiedz K, Buggisch H, Willenbacher N. Extensional rheology of concentrated emulsions as probed by capillary breakup elongational theometry (CaBER). *Rheol Acta* 2011;**49**:1103-1116.

[9] Akay G. Flow-induced phase inversion in the intensive processing of concentrated emulsions, *Chem Eng Sci* 1998;**53**(2):203-223.

[10] Trouton FT. On the coefficient of viscous traction and its relation to that of viscosity. *Proc Roy Soc* 1906;**l**:426-440.

[11] Chhabra RP, Richardson JF. *Non-Newtonian Flow and Applied Rheology*. Elsevier Ltd; 2008.

[12] Frank FC, Keller A, Mackley MR. Polymer chain extension produced by impinging jets and its effect on polyethylene solution. *Polymer* 1971;**12**:467-473.

[13] Mackley MR, Keller A. Flow induced polymer chain extension and its relation to fibrous crystallization. *Phil Trans Roy Soc*. London A. 1975;**278**:29-66.

[14] Keller A, Müller AJ, Odell JA. Entanglements in semi-dilute solutions as revealed by elongational flow studied. *Polymer and Colloid* 1987;**75**:179-200.

[15] Chow A, Müller AJ, Odell JA. Entanglements in polymer solutions under elongational flow: a combined study of chain stretching, flow velocimetry, and elongational viscosity. *Macromolecules* 1988;**21**:250-256.

[16] Fuller GG, Cathey CA, Hubbard B, Zebrowski BE. Extensional viscosity measurements for low-viscosity fluids. *J Rheol* 1987;**31**:235-249.

[17] Dontula P, Pasquali M, Scriven LE, Macosko ChW. Can extensional viscosity be measured with opposed-nozzle devices?. *Rheol Acta* 1997;**36**:429-448.